

**NEW JERSEY DEPARTMENT OF ENVIRONMENTAL PROTECTION**  
**BUREAU OF RELEASE PREVENTION**  
**TOXIC CATASTROPHE PREVENTION ACT (TCPA) PROGRAM**

**Guidance on Hazard Assessment for Reactive Hazard Substances (RHSs) and RHS**  
**Mixtures**

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## Introduction

N.J.A.C. 7:31-2.2(a) requires the owner or operator (o/o) of a facility handling a reactive hazard substance (RHS) listed in N.J.A.C. 7:31-6.3(a), Table I, Part D, Group I, or RHS mixture determined pursuant to N.J.A.C. 7:31-6.3(b) to perform a hazard assessment and report in the Risk Management Plan one worst-case scenario and one alternative release scenario. The Bureau has prepared this guidance document to help the o/o estimate the endpoint distance for the RHS and RHS mixture worst-case and alternative release scenarios.

This document provides guidance to the o/o of processes subject to the New Jersey Department of Environmental Protection (DEP) TCPA Program rules. This document does not substitute for TCPA's regulations, nor is it a regulation itself. Thus, it cannot impose legally binding requirements on DEP or the regulated community, and may not apply to a particular situation based upon the circumstances. This guidance does not constitute final agency action, and DEP may change it in the future, as appropriate.

## Hazard Assessment

When performing the hazard assessment for the worst-case scenario, the o/o of a facility must estimate the endpoint distance using an overpressure endpoint of 1 psi and the worst-case release quantity. The worst-case release quantity must be based on the maximum capacity of the process vessel containing the RHS or RHS mixture, and administrative controls that limit the maximum quantity in the process vessel must not be taken into account. For the alternative release scenario, the o/o of a facility may consider the use of thermal radiation and lower flammability endpoints in addition to that of the overpressure endpoint.

To conduct the hazard assessment for an overpressure scenario, the o/o may use a modification of the EPA's TNT-equivalency method equations found in EPA's "Risk Management Program Guidance for Offsite Consequence Analysis," March 2009, Appendix C, Flammable Substances, Section C.1: Equation for Estimation of Distance to 1 psi Overpressure for Vapor Cloud Explosions [1]. A generic form of EPA's equation C-2 is:

$$D = 0.0081 \times [y \times W \times (HC_f/HC_{TNT})]^{1/3} \quad \text{Equation 1}$$

where: D = distance of 1 psi overpressure, miles  
y = yield factor, percentage of the flammable vapor in the cloud assumed to participate in the explosion  
W = weight of the flammable substance, pounds  
HC<sub>f</sub> = heat of combustion of the flammable substance, cal/g  
HC<sub>TNT</sub> = heat of explosion of trinitrotoluene (TNT), (1,119 cal/g)

In equation C-2 of the EPA guidance, y is assumed to be 10% (0.10) for a vapor cloud explosion. The TCPA rule at N.J.A.C. 7:31-2.2(b)3ii&iii requires that y is assumed to be 100% (1.0) for an RHS and RHS mixture since the substance is contained within a vessel.

For an RHS and RHS mixture, the heat of reaction,  $H_R$ , can be used to replace the heat of combustion term in Equation 1, which then simplifies to be:

$$D = 0.0081 \times [W \times (H_R/1,119)]^{1/3} \quad \text{Equation 2}$$

where:  $D$  = distance of 1 psi overpressure, miles  
 $W$  = weight of the RHS or RHS mixture, pounds  
 $H_R$  = heat of reaction of the RHS or RHS mixture, cal/g

Heat of reaction is defined at N.J.A.C. 7:31-1.5 as “the change in the amount of heat energy of the substances contained in a process vessel that occurs during a chemical reaction expressed as calories per gram; or specifically, the energy content of the reaction products minus the energy content of the reactants. The heat of reaction includes heat energies such as the heat of decomposition, heat of explosion or heat of combustion depending on the chemical reaction(s) taking place.”

### **Heat of Reaction for RHSs Listed in N.J.A.C. 7:31-6.3(a) Table I, Part D, Group I**

For the hazard assessment of Group I RHSs, the heat of decomposition should be used as the heat of reaction value in Equation 2. The heat of decomposition can be obtained from literature review, calculation, or calorimetry testing. N.J.A.C.7:31-2.2(b)3iii states that 28 percent of the heat of combustion may be used as an approximation if the detailed heat of reaction data is not available. In the TNT equivalency method used by the EPA, the explosive energy of a reactive hazard substance is related to an equivalent amount of TNT. The “energy of explosion,” which is the amount of energy released when a substance explodes, is not available for many of the listed RHSs in technical sources. The value of 28% of the heat of combustion was selected because the ratio of energy of explosion to heat of combustion for many highly reactive substances, such as TNT, is 28%.

Table 1 of this guidance presents the heat of combustion values that may be used to make this estimation. Table 2 of this guidance presents the heat of decomposition values of some Group I RHSs that may be used as the heat of reaction value. (Note: the heat of decomposition is not multiplied by 28% to estimate the heat of reaction value used in Equation 2.) The o/o should maintain reference documentation for the heat of reaction value that is used.

### **Heat of Reaction for RHS Mixtures**

Calorimetric testing, engineering calculation, or literature review may be used to determine the heat of reaction for the RHS mixture. See the Department’s “Guidance for Determining the Applicability of the TCPA Program Rules,” Section II.C, for more detailed information on determining the heat of reaction of an RHS mixture.

For the worst-case scenario, you must express the final heat of reaction value for the RHS mixture in units of calories per gram of RHS mixture excluding any non-reacting substances. For the alternative release scenario, you may include the quantity of non-reacting substances such as solvents that are included in the vessel with the RHS mixture to express the heat of reaction value.

### **Release Quantity Weight of RHS or RHS Mixture for the Hazard Assessment**

Pursuant to N.J.A.C. 7:31-2.2(b)2, the o/o must use the maximum capacity of the largest process vessel containing an RHS or RHS mixture for the worst-case scenario release quantity; administrative controls that limit the maximum quantity are not allowed to be taken into account. For the alternative release scenario for an RHS or RHS mixture, administrative controls that are employed to limit the quantity of an RHS or RHS mixture in a process vessel may be taken into account. See the Department's "Guidance for Determining the Applicability of the TCPA Program Rules," Section II.B.2, for more detailed information on determining the weight capacity of a process vessel for an RHS mixture.

### **Alternative Release Scenario Analysis for RHSs or RHS Mixtures**

Depending on the release scenario, the o/o of a covered process may use the overpressure endpoint of 1 psi, thermal radiation endpoint of 5 kW/m<sup>2</sup> for 40 seconds, or the lower flammability limit.

In general, one of the scenarios from a process hazard analysis should be selected for the alternative release scenario analysis. For scenarios that may result in an explosion, the o/o may use Equation 2 to estimate the distance to the 1 psi overpressure endpoint.

The o/o may construct an event tree to obtain different outcomes of the released RHS or RHS Mixture, such as boiling liquid expanding vapor explosion, confined and unconfined vapor cloud explosion, flash fire, jet fire, and pool fire. Such event trees are shown in Figures 8.13 and 8.14 of reference [2]. The o/o may use the procedures outlined for flammable substance alternative release scenarios in the EPA, Chemical Emergency Preparedness and Prevention Office, "Risk Management Program Guidance for Offsite Consequence Analysis," EPA 550-B-99-009, March 2009 [3].

### **Example 1**

#### **Determining the worst-case scenario endpoint distance for a Group I RHS**

Scenario: Failure of a storage tank that stores uninhibited di-tert-butyl peroxide.

The maximum capacity of a storage tank that stores uninhibited di-tert-butyl peroxide is 100,000 pounds. The o/o applies administrative control to limit the inventory held in the storage tank to 50,000 pounds of the uninhibited di-tert-butyl peroxide at any time. However, this administrative control that limits the maximum quantity in the storage tank must not be taken into account for the worst-case scenario analysis. From Table 1, the heat of combustion for di-tert-butyl peroxide is 8,727 cal/g.

Use Equation 2 to estimate the distance to 1.0 psi as follows:

Weight of reactive hazard substance,  $W = 100,000$  pounds

Heat of Reaction,  $H_R$ , cal/g:

From Table 1, the heat of combustion = 8,727 cal/g

Estimated  $H_R = 28\% \times \text{heat of combustion} = 28\% \times 8,727 = 2,444$  cal/g

Using Equation 2,

$$D = 0.0081 \times [W \times (H_R/1,119)]^{1/3}$$

where:  $D =$  distance of 1 psi overpressure, miles

$W =$  weight of the RHS or RHS mixture, pounds

$H_R =$  heat of reaction of the RHS or RHS mixture, cal/g

$$D = 0.0081 \times [100,000 \times (2,444/1,119)]^{1/3} = 0.49 \text{ miles}$$

### **Example 2**

#### **Determining the alternative-case scenario endpoint distance for a Group I RHS**

Scenario: Failure of a storage tank that stores uninhibited di-tert-butyl peroxide.

The maximum capacity of a storage tank that stores uninhibited di-tert-butyl peroxide is 100,000 pounds. The o/o applies administrative control to limit the inventory held in the storage tank to 50,000 pounds of the uninhibited di-tert-butyl peroxide at any time. From Table 1, the heat of combustion for di-tert-butyl peroxide is 8,727 cal/g.

Use Equation 2 to estimate the distance to 1.0 psi as follows:

Weight of reactive hazard substance,  $W = 50,000$  pounds taking into account administrative controls.

Heat of Reaction,  $H_R$ , cal/g:

From Table 1, the heat of combustion = 8,727 cal/g

Estimated  $H_R = 28\% \times \text{heat of combustion} = 28\% \times 8,727 = 2,444$  cal/g

Using Equation 2,

$$D = 0.0081 \times [W \times (H_R/1,119)]^{1/3}$$

where: D = distance of 1 psi overpressure, miles  
W = weight of the RHS or RHS mixture, pounds  
H<sub>R</sub> = heat of reaction of the RHS or RHS mixture, cal/g

$$D = 0.0081 \times [50,000 \times (2,444/1,119)]^{1/3} = 0.39 \text{ miles}$$

### **Example 3**

#### **Determining the worst-case scenario endpoint distance for an RHS mixture**

Scenario: Runaway reaction and failure of a vinyl chloride monomer (VCM) polymerization reactor.

Assume that a runaway reaction and catastrophic failure occurs for a 4,000-gallon (534.76 ft<sup>3</sup>) reactor used for suspension polymerization of vinyl chloride monomer. The following parameters apply to the polymerization reactor: the reactor mainly contains 43% vinyl chloride monomer and 57% water, an administrative control dictates that the reactor be run at 50% capacity, the estimated average density of the reactor contents is 52.6 lbs./ft<sup>3</sup>, and the documented heat of polymerization of vinyl chloride monomer is -729 Btu/lb. of VCM.

First, estimate the reaction mass, W (pounds) as follows:

$$W = \rho \eta V$$

where:

ρ = average density of the reactor contents, lb./ft<sup>3</sup> = 52.6

V = maximum reactor volume, ft<sup>3</sup> = 534.76

η = 100 percent of the reactor filled = 1.0 (Note that an administrative control that limits the maximum quantity in the reactor must not be taken into account for the worst-case scenario analysis)

$$W = 52.6 \times 1.0 \times 534.76 = 28,128 \text{ pounds}$$

Second, estimate the heat of reaction of the RHS mixture, H<sub>R</sub> (cal/g), as follows:

$$\begin{aligned} H_R \text{ (cal/g)} &= -729 \text{ Btu/lb. of VCM} \times (251.96 \text{ cal/Btu}) \times (1 \text{ pound}/454\text{g}) \\ &= -405 \text{ cal/g} \end{aligned}$$

Using Equation 2,

$$D = 0.0081 \times [W \times (H_R/1,119)]^{1/3}$$

where: D = distance of 1 psi overpressure, miles  
W = weight of the RHS or RHS mixture, pounds  
H<sub>R</sub> = heat of reaction of the RHS or RHS mixture, cal/g

$$D = 0.0081 \times [28,128 \times (405/1,119)]^{1/3} = 0.18 \text{ miles}$$

#### **Example 4**

#### **Determining the alternative-case scenario endpoint distance for an RHS mixture**

Scenario: Runaway reaction and failure of a vinyl chloride monomer (VCM) polymerization reactor.

Assume that a runaway reaction and catastrophic failure occurs for a 4,000-gallon (534.76 ft<sup>3</sup>) reactor used for suspension polymerization of vinyl chloride monomer. The following parameters apply to the polymerization reactor: the reactor mainly contains 43% vinyl chloride monomer and 57% water, an administrative control dictates that the reactor be run at 50% capacity, the estimated average density of the reactor contents is 52.6 lbs./ft<sup>3</sup>, and the documented heat of polymerization of vinyl chloride monomer is -729 Btu/lb. of VCM.

First, estimate the reaction mass, W (pounds) as follows:

$$W = \rho \eta V$$

where:

$$\rho = \text{average density of the reactor contents, lb./ft}^3 = 52.6$$

$$V = \text{maximum reactor volume, ft}^3 = 534.76$$

$$\eta = 50 \text{ percent of the reactor filled} = 0.5$$

$$W = 52.6 \times 0.50 \times 534.76 = 14,064 \text{ pounds}$$

Second, estimate the heat of reaction of the RHS mixture, H<sub>R</sub> (cal/g). For the alternative case, the heat of reaction can be expressed taking into account the amount of non-reacting substances (in this example water).

$$\begin{aligned} H_R \text{ (cal/g of VCM)} &= -729 \text{ Btu/lb. of VCM} \times (251.96 \text{ cal/Btu}) \times (1 \text{ pound}/454\text{g}) \\ &= -405 \text{ cal/g of VCM} \end{aligned}$$

$$\begin{aligned} H_R \text{ (cal/g of total contents)} &= -405 \text{ cal/g of VCM} \times (43 \text{ g of VCM}/100 \text{ g of total contents}) \\ &= -174 \text{ cal/g of total contents} \end{aligned}$$

Using Equation 2,

$$D = 0.0081 \times [W \times (H_R/1,119)]^{1/3}$$

where: D = distance of 1 psi overpressure, miles

W = weight of the RHS or RHS mixture, pounds

H<sub>R</sub> = heat of reaction of the RHS or RHS mixture, cal/g

$$D = 0.0081 \times [14,064 \times (174/1,119)]^{1/3} = 0.11 \text{ miles}$$



### **Example 5**

#### **Determining the alternative-case scenario endpoint distance for a Group I RHS**

Scenario: Leak of ethyl nitrite from a fill line during tank unloading.

Assume that the covered process is located in a rural area. One of the likely scenarios from a hazard analysis study is a leak of ethyl nitrite from a fill line during tank unloading. Also, assume that the release rate was determined to be 50 pounds per minute. From the safety information or process safety information, the lower flammable limit (LFL) for ethyl nitrite is 4% (120 mg/l), and the vapor density is greater than that of air (dense gas). One of the outcomes of the release is a dispersion of the ethyl nitrite to its LFL that may result in thermal radiation effects. From Table 28 of reference [3], on the first column locate the row that contains the release rate of 50 pounds per minute (select release rate <1500 pounds per minute) and on the second row locate the column that contains the LFL of 120 mg/l (select LFL >100 mg/l column). The intersection of the row that contains <1500 lbs./min and the column that contains >100 mg/l is the distance to the LFL endpoint. This distance is less than 0.1 miles (528 ft).

**Table 1: Heat of Combustion for Part D, Group I Reactive Hazard Substances**

CAS Number	Chemical Name	Heat of Combustion (cal/g)	Data Source Reference
110-22-5	Acetyl peroxide	3839	NIST WEBBOOK
97-00-7	Chlorodinitrobenzenes	3147	ASTM CHETAH
80-15-9	Cumene hydroperoxide	8016	NIST WEBBOOK
94-36-0	Dibenzoyl peroxide	6481	NIST WEBBOOK
628-37-5	Diethyl peroxide	7372	NIST WEBBOOK
105-64-6	Diisopropyl peroxydicarbonate	4453	ASTM CHETAH
51-28-5	Dinitrophenol	3501	NIST WEBBOOK
35860-51-6	Dinitroresorcinol	3220	ASTM CHETAH
2217-06-3	Dipicryl sulfide	5961	ASTM CHETAH
110-05-4	Di-tert-Butyl peroxide	8727	NIST WEBBOOK
821-08-9	Divinyl acetylene	10525	ASTM CHETAH
625-58-1	Ethyl nitrate	3441	NIST WEBBOOK
109-95-5	Ethyl nitrite	4105	ASTM CHETAH
87-33-2	Isosorbide dinitrate	2817	ASTM CHETAH
7803-54-5	Magnesium diamide	4190	ASTM CHETAH
99-65-0	m-Dinitrobenzene	4140	NIST WEBBOOK
55-63-0	Nitroglycerin	1625	KIRK Vol. 9 p573
75-52-5	Nitromethane	2779	NIST WEBBOOK
528-29-0	o-Dinitrobenzene	4166	NIST WEBBOOK
100-25-4	p-Dinitrobenzene	4115	NIST WEBBOOK
79-21-0	Peracetic acid	2928	ASTM CHETAH
88-89-1	Picric acid	2869	ASTM CHETAH
106-96-7	Propargyl bromide	3513	ASTM CHETAH
146-84-9	Silver picrate	1887	ASTM CHETAH
75-91-2	Tert-Butyl hydroperoxide	7186	NIST WEBBOOK
507-40-4	Tert-Butyl hypochlorite	5077	ASTM CHETAH
99-35-4	Trinitrobenzene as 1,3,5	3087	NIST WEBBOOK

**Table 2: Heat of Decomposition for Part D, Group I Reactive Hazard Substances**

CAS Number	Chemical Name	Heat of Decomposition (cal/g)	Data Source Reference
15512-36-4	Calcium dithionite	1220	ASTM CHETAH
14293-73-3	Potassium dithionite	770	ASTM CHETAH
7775-14-6	Sodium dithionite	874	ASTM CHETAH

## REFERENCES

[1] EPA, Chemical Emergency Preparedness and Prevention Office, "Risk Management Program Guidance for Offsite Consequence Analysis", March 2009, Appendix C.

[2] Center for Chemical Process Safety (CCPS) of the American Institute of Chemical Engineers, Guidelines for Chemical Process Quantitative Risk Analysis, 1989.

[3] EPA, Chemical Emergency Preparedness and Prevention Office, "Risk Management Program Guidance for Offsite Consequence Analysis," EPA 550-B-99-009, March 2009, pages 10-22.